Supporting Information - Inducing high ionic conductivity in the lithium superionic argyrodites $Li_{6+x}P_{1-x}Ge_xS_5I$ for all-solid-state batteries

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Table S 1. Crystallographic data of Li_6PS_5I, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of Li_6PS_5I. Refined parameters are shown with errors in brackets.

Li_6PS_5I structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.14516(7) Å; 3.56 % Li_2S R_{wp} = 3.40 %; *S* = 2.03						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2956</u>	<u>0.0266</u>	<u>0.7044</u>	<u>0.391</u>	4
Li2	24*g*	0.25	<u>0.018</u>	0.75	<u>0.219</u>	4
I1	4*a*	0	0	1	1.000(5)	2.55(5)
I2	4*d*	0.25	0.25	0.75	0.000(5)	1.9(2)
P1	4*b*	0	0	0.5	1	1.21(9)
S1	4*d*	0.25	0.25	0.75	1.000(5)	1.9(2)
S2	16*e*	0.1158(2)	-0.1158(2)	0.6158(2)	1	2.55(5)
S3	4*a*	0	0	1	0.000(5)	1.92(7)

Table S 2. Crystallographic data of $Li_{6.1}P_{0.9}Ge_{0.1}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.15}P_{0.85}Ge_{0.15}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.1}P_{0.9}Ge_{0.1}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.16695(9) Å; 2.13% Li_4GeS_4; 1.09 % Li_2S R_{wp} = 3.23 %; *S* = 1.31						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2961</u>	<u>0.0252</u>	<u>0.7039</u>	<u>0.377</u>	4
Li2	24*g*	0.25	<u>0.0158</u>	0.75	<u>0.27</u>	4
I1	4*a*	0	0	1	1.000(6)	3.65(7)
I2	4*d*	0.25	0.25	0.75	0.000(6)	2.8(2)
P1	4*b*	0	0	0.5	0.918(9)	2.0(2)
Ge1	4*b*	0	0	0.5	0.082(9)	2.0(2)
S1	4*d*	0.25	0.25	0.75	1.000(6)	2.8(2)
S2	16*e*	0.1170(2)	-0.1170(2)	0.6170(2)	1	2.27(8)
S3	4*a*	0	0	1	0.000(6)	2.8(2)

Table S 3. Crystallographic data of $Li_{6.15}P_{0.85}Ge_{0.15}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.15}P_{0.85}Ge_{0.15}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.15}P_{0.85}Ge_{0.15}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.18054(8) Å; 1.49 % Li_2S R_{wp} = 3.82 %; *S* = 1.60						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2961</u>	<u>0.0252</u>	<u>0.7039</u>	<u>0.377</u>	4
Li2	24*g*	0.25	<u>0.0158</u>	0.75	<u>0.27</u>	4
I1	4*a*	0	0	1	1.000(5)	3.85(5)
I2	4*d*	0.25	0.25	0.75	0.000(5)	2.4(2)
P1	4*b*	0	0	0.5	0.849(8)	1.77(12)
Ge1	4*b*	0	0	0.5	0.151(5)	1.77(12)
S1	4*d*	0.25	0.25	0.75	1.000(5)	2.4(2)
S2	16*e*	0.1177(2)	-0.1177(2)	0.6177(2)	1	2.44(6)
S3	4*a*	0	0	1	0.000(5)	3.85(5)

Table S 4. Crystallographic data of $Li_{6.2}P_{0.8}Ge_{0.2}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.25}P_{0.75}Ge_{0.25}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.2}P_{0.8}Ge_{0.2}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.18473(10) Å; 2.95 % Li_2S; 2.21 % LiI R_{wp} = 3.86 %; *S* = 1.62						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2971</u>	<u>0.0255</u>	<u>0.7029</u>	<u>0.359</u>	4
Li2	24*g*	0.25	<u>0.017</u>	0.75	<u>0.33</u>	4
I1	4*a*	0	0	1	0.980(7)	4.19(7)
I2	4*d*	0.25	0.25	0.75	0.020(7)	3.6(3)
P1	4*b*	0	0	0.5	0.765(14)	3.6(2)
Ge1	4*b*	0	0	0.5	0.235(14)	3.6(2)
S1	4*d*	0.25	0.25	0.75	0.980(7)	3.6(3)
S2	16*e*	0.1168(2)	-0.1168(2)	0.6168(2)	1	3.09(9)
S3	4*a*	0	0	1	0.020(7)	4.19(7)

Table S 5. Crystallographic data of $Li_{6.25}P_{0.75}Ge_{0.25}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.25}P_{0.75}Ge_{0.25}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.25}P_{0.75}Ge_{0.25}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.19307(8) Å; 2.15 % Li_4GeS_4; 1.71% LiI R_{wp} = 3.43 %; *S* = 1.39						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2971</u>	<u>0.0255</u>	<u>0.7029</u>	<u>0.359</u>	4
Li2	24*g*	0.25	<u>0.017</u>	0.75	<u>0.33</u>	4
I1	4*a*	0	0	1	0.986(6)	3.82(6)
I2	4*d*	0.25	0.25	0.75	0.014(6)	3.2(2)
P1	4*b*	0	0	0.5	0.735(11)	2.9(2)
Ge1	4*b*	0	0	0.5	0.265(11)	2.9(2)
S1	4*d*	0.25	0.25	0.75	0.986(6)	3.2(2)
S2	16*e*	0.1177(2)	-0.1177(2)	0.6177(2)	1	2.80(8)
S3	4*a*	0	0	1	0.014(6)	3.82(6)

Table S 6. Crystallographic data of $Li_{6.3}P_{0.7}Ge_{0.3}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.30}P_{0.70}Ge_{0.30}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.3}P_{0.7}Ge_{0.3}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.20585(9) Å; 6.19 % Li_4GeS_4 R_{wp} = 3.22 %; *S* = 1.33						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2968</u>	<u>0.0234</u>	<u>0.7032</u>	<u>0.358</u>	4
Li2	24*g*	0.25	<u>0.0156</u>	0.75	<u>0.34</u>	4
I1	4*a*	0	0	1	0.990(6)	4.22(7)
I2	4*d*	0.25	0.25	0.75	0.010(6)	2.6(2)
P1	4*b*	0	0	0.5	0.632(11)	2.9(2)
Ge1	4*b*	0	0	0.5	0.368(11)	2.9(2)
S1	4*d*	0.25	0.25	0.75	0.990(6)	2.6(2)
S2	16*e*	0.1178(2)	-0.1178(2)	0.6178(2)	1	2.84(8)
S3	4*a*	0	0	1	0.010(6)	4.22(7)

Table S 7. Crystallographic data of $Li_{6.4}P_{0.6}Ge_{0.4}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.30}P_{0.70}Ge_{0.30}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.4}P_{0.6}Ge_{0.4}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.22972(7) Å; 1.87 % Li_4GeS_4; 1.06 % Li_2S R_{wp} = 3.18 %; *S* = 1.26						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2968</u>	<u>0.0234</u>	<u>0.7032</u>	<u>0.358</u>	4
Li2	24*g*	0.25	<u>0.0156</u>	0.75	<u>0.34</u>	4
I1	4*a*	0	0	1	0.990(5)	4.89(7)
I2	4*d*	0.25	0.25	0.75	0.010(5)	2.7(2)
P1	4*b*	0	0	0.5	0.528(11)	2.81(14)
Ge1	4*b*	0	0	0.5	0.472(11)	2.81(14)
S1	4*d*	0.25	0.25	0.75	0.990(5)	2.7(2)
S2	16*e*	0.1184(2)	-0.1184(2)	0.6184(2)	1	2.95(8)
S3	4*a*	0	0	1	0.010(5)	4.89(7)

Table S 8. Crystallographic data of $Li_{6.5}P_{0.5}Ge_{0.5}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.60}P_{0.40}Ge_{0.60}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.5}P_{0.5}Ge_{0.5}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.24314(7) Å; 2.68 % Li_4GeS_4; 2.60 % LiI; 1.53 % Li_2S R_{wp} = 2.94 %; *S* = 1.47						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2991</u>	<u>0.0222</u>	<u>0.7009</u>	<u>0.351</u>	4
Li2	24*g*	0.25	<u>0.0119</u>	0.75	<u>0.41</u>	4
I1	4*a*	0	0	1	0.968(6)	4.09(6)
I2	4*d*	0.25	0.25	0.75	0.032(6)	3.1(2)
P1	4*b*	0	0	0.5	0.492(11)	2.55(13)
Ge1	4*b*	0	0	0.5	0.508(11)	2.55(13)
S1	4*d*	0.25	0.25	0.75	0.968(6)	3.1(2)
S2	16*e*	0.1198(2)	-0.1198(2)	0.6198(2)	1	2.88(8)
S3	4*a*	0	0	1	0.032(6)	4.09(6)

Table S 9. Crystallographic data of $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.60}P_{0.40}Ge_{0.60}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.24314(7) Å; 1.63 % LiI R_{wp} = 3.19 %; *S* = 1.64						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2991</u>	<u>0.0222</u>	<u>0.7009</u>	<u>0.351</u>	4
Li2	24*g*	0.25	<u>0.0119</u>	0.75	<u>0.41</u>	4
I1	4*a*	0	0	1	0.969(6)	4.84(7)
I2	4*d*	0.25	0.25	0.75	0.031(6)	3.6(2)
P1	4*b*	0	0	0.5	0.318(12)	3.00(13)
Ge1	4*b*	0	0	0.5	0.682(12)	3.00(13)
S1	4*d*	0.25	0.25	0.75	0.969(6)	3.6(2)
S2	16*e*	0.1200(2)	-0.1200(2)	0.6200(2)	1	2.88(7)
S3	4*a*	0	0	1	0.031(6)	4.84(7)

Table S 10. Crystallographic data of $Li_{6.7}P_{0.3}Ge_{0.7}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.60}P_{0.40}Ge_{0.60}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.7}P_{0.3}Ge_{0.7}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.2851(9) Å; 1.93 % Li_2S; 2.29 % LiI R_{wp} = 3.19 %; *S* = 1.29						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2991</u>	<u>0.0222</u>	<u>0.7009</u>	<u>0.351</u>	4
Li2	24*g*	0.25	<u>0.0119</u>	0.75	<u>0.41</u>	4
I1	4*a*	0	0	1	0.944(7)	4.12(7)
I2	4*d*	0.25	0.25	0.75	0.056(7)	3.8(2)
P1	4*b*	0	0	0.5	0.227(13)	2.65(13)
Ge1	4*b*	0	0	0.5	0.773(13)	2.65(13)
S1	4*d*	0.25	0.25	0.75	0.944(7)	3.8(2)
S2	16*e*	0.1216(2)	-0.1216(2)	0.6216(2)	1	2.74(8)
S3	4*a*	0	0	1	0.056(7)	4.12(7)

Table S 11. Crystallographic data of $Li_{6.8}P_{0.2}Ge_{0.8}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.60}P_{0.40}Ge_{0.60}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.8}P_{0.2}Ge_{0.8}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.2998(2) Å; 9.72 % Li_4GeS_4; 8.07 % LiI R_{wp} = 4.61 %; *S* = 2.30						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2991</u>	<u>0.0222</u>	<u>0.7009</u>	<u>0.351</u>	4
Li2	24*g*	0.25	<u>0.0119</u>	0.75	<u>0.41</u>	4
I1	4*a*	0	0	1	0.927(13)	4.4(2)
I2	4*d*	0.25	0.25	0.75	0.073(13)	4.5(5)
P1	4*b*	0	0	0.5	0.21(2)	2.3(2)
Ge1	4*b*	0	0	0.5	0.79(2)	2.3(2)
S1	4*d*	0.25	0.25	0.75	0.927(13)	4.5(5)
S2	16*e*	0.1216(4)	-0.1216(4)	0.6216(4)	1	2.80(14)
S3	4*a*	0	0	1	0.073(13)	4.4(2)

Table S 12. Crystallographic data of $Li_{6.9}P_{0.1}Ge_{0.9}S_5I$, with Lithium correlated parameters (underlined) fixed to parameters retrieved from neutron data of $Li_{6.60}P_{0.40}Ge_{0.60}S_5I$. Refined parameters are shown with errors in brackets.

$Li_{6.9}P_{0.1}Ge_{0.9}S_5I$ structure from X-ray powder diffraction data (space group F-43m); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2 (Cu-$K_{\alpha2}$) = 1.5444 Å *a* = 10.2978(7) Å; 32.35 % Li_4GeS_4; 25.11 % LiI R_{wp} = 10.5 %; *S* = 5.29						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	<u>0.2991</u>	<u>0.0222</u>	<u>0.7009</u>	<u>0.351</u>	4
Li2	24*g*	0.25	<u>0.0119</u>	0.75	<u>0.41</u>	4
I1	4*a*	0	0	1	0.87(8)	4.8(7)
I2	4*d*	0.25	0.25	0.75	0.13(8)	7(2)
P1	4*b*	0	0	0.5	0.12(12)	4.7(9)
Ge1	4*b*	0	0	0.5	0.88(12)	4.7(9)
S1	4*d*	0.25	0.25	0.75	0.87(8)	7(2)
S2	16*e*	0.118(2)	-0.118(2)	0.618(2)	1	2.3(7)
S3	4*a*	0	0	1	0.13(8)	4.8(7)

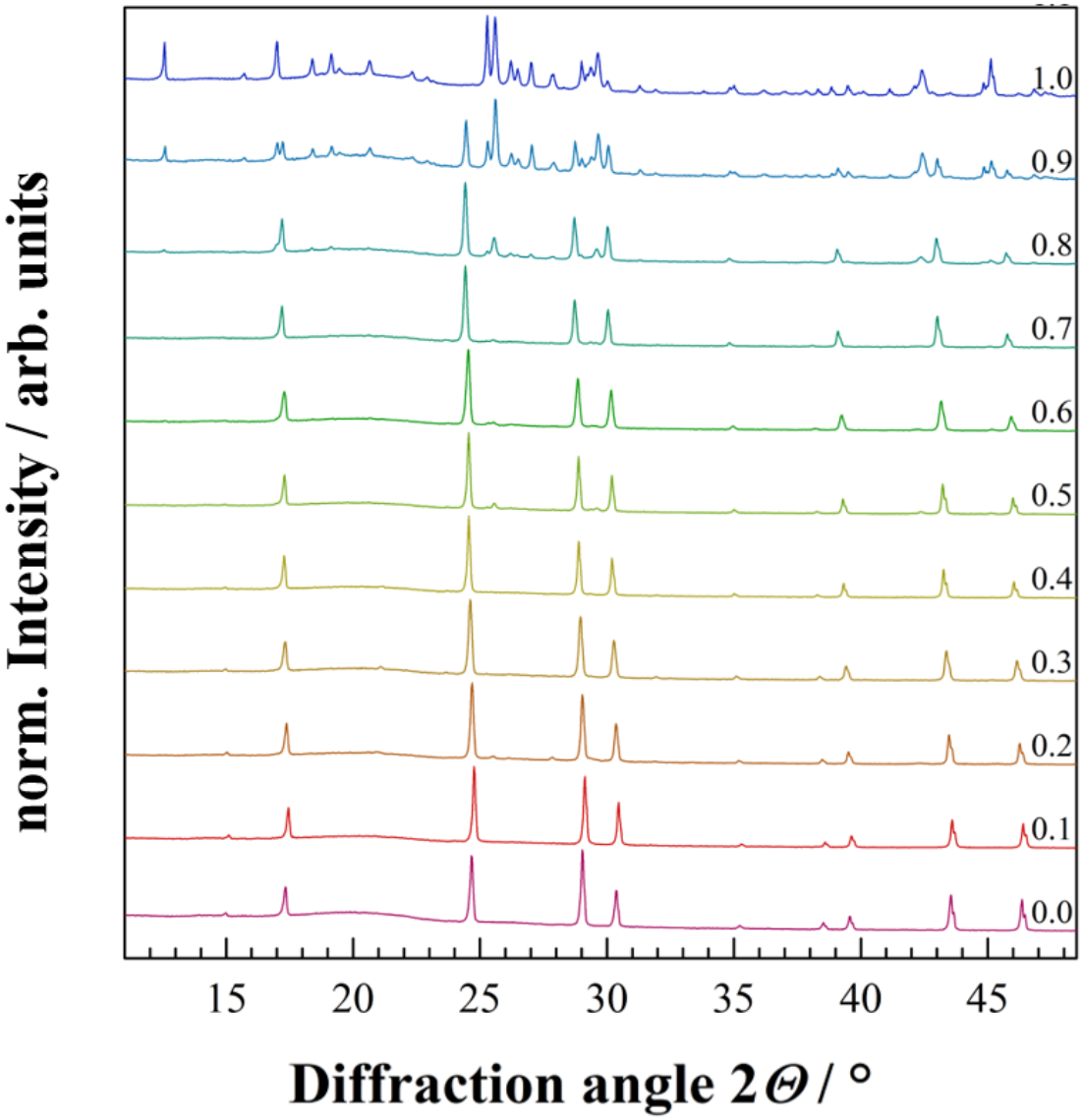

Figure S 1: X-ray diffraction patterns of the compositions $Li_{6+x}P_{1-x}Ge_xS_5I$ in comparison.

Table S 13. Crystallographic data of $Li_{6.15}P_{0.85}Ge_{0.15}S_5I$ from neutron diffraction

$Li_{6.15}P_{0.85}Ge_{0.15}S_5I$ structure from neutron diffraction data (space group F-43m); λ (Ge(551)) = 1.54817 Å *a* = 10.17422(10) Å; 1.44 % LiI R_{wp} = 3.10 %; *S* = 1.51						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	0.2961(8)	0.0252(5)	0.7039(8)	0.377(12)	2.3(2)
Li2	24*g*	0.25	0.015(2)	0.75	0.27(2)	1.3(4)
I1	4*a*	0	0	1	1.000(9)	2.25(5)
I2	4*d*	0.25	0.25	0.75	0.000(9)	1.28(6)
P1	4*b*	0	0	0.5	0.862(12)	0.99(5)
Ge1	4*b*	0	0	0.5	0.138(12)	0.99(5)
S1	4*d*	0.25	0.25	0.75	1.000(9)	1.28(6)
S2	16*e*	0.1171(2)	-0.1171(2)	0.6171(2)	1	1.31(5)
S3	4*a*	0	0	1	0.000(9)	2.25(5)

Table S 14. Crystallographic data of $Li_{6.25}P_{0.75}Ge_{0.25}S_5I$ from neutron diffraction

$Li_{6.25}P_{0.75}Ge_{0.25}S_5I$ structure from neutron diffraction data (space group F-43m); λ (Ge(551)) = 1.54817 Å *a* = 10.19943(12) Å; 3.13 % Li_2S; 4.80 % LiI R_{wp} = 3.31 %; *S* = 1.61						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	0.2971(9)	0.0255(7)	0.7029(9)	0.35(2)	2.4(2)
Li2	24*g*	0.25	0.017(2)	0.75	0.33(3)	2.1(5)
I1	4*a*	0	0	1	0.973(10)	2.43(6)
I2	4*d*	0.25	0.25	0.75	0.027(10)	1.52(8)
P1	4*b*	0	0	0.5	0.706(14)	1.00(5)
Ge1	4*b*	0	0	0.5	0.294(14)	1.00(5)
S1	4*d*	0.25	0.25	0.75	0.973(10)	1.52(8)
S2	16*e*	0.1180(2)	-0.1180(2)	0.6180(2)	1	1.30(6)
S3	4*a*	0	0	1	0.027(10)	2.43(6)

Table S 15. Crystallographic data of $Li_{6.3}P_{0.7}Ge_{0.3}S_5I$ from neutron diffraction

$Li_{6.3}P_{0.7}Ge_{0.3}S_5I$ structure from neutron diffraction data (space group F-43m); λ (Ge(551)) = 1.54817 Å *a* = 10.20701(9) Å; 1.77 % LiI R_{wp} = 3.01 %; *S* = 1.47						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	0.2968(8)	0.0234(6)	0.7032(8)	0.358(11)	2.8(2)
Li2	24*g*	0.25	0.015(2)	0.75	0.34(2)	1.8(3)
I1	4*a*	0	0	1	0.987(9)	2.57(4)
I2	4*d*	0.25	0.25	0.75	0.013(9)	1.40(6)
P1	4*b*	0	0	0.5	0.689(7)	1.07(4)
Ge1	4*b*	0	0	0.5	0.311(7)	1.07(4)
S1	4*d*	0.25	0.25	0.75	0.013(9)	2.57(4)
S2	16*e*	0.1182(2)	-0.1182(2)	0.6182(2)	1	1.30(5)
S3	4*a*	0	0	1	0.987(9)	2.57(4)

Table S 16. Crystallographic data of $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ from neutron diffraction

$Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ structure from neutron diffraction data (space group F-43m); λ (Ge(551)) = 1.54817 Å *a* = 10.26480(10) Å; 3.40 % LiI R_{wp} = 3.24 %; *S* = 1.58						
Atom	**Wyckoff Site**	**x/*a***	**y/*b***	**z/*c***	**Occ.**	**B_{eq}/Å²**
Li1	48*h*	0.2991(9)	0.0222(8)	0.7009(9)	0.351(12)	3.5(2)
Li2	24*g*	0.25	0.011(2)	0.75	0.41(2)	1.9(3)
I1	4*a*	0	0	1	0.937(8)	2.95(5)
I2	4*d*	0.25	0.25	0.75	0.063(9)	1.54(6)
P1	4*b*	0	0	0.5	0.334(14)	1.30(4)
Ge1	4*b*	0	0	0.5	0.666(14)	1.30(4)
S1	4*d*	0.25	0.25	0.75	0.937(9)	1.54(6)
S2	16*e*	0.1195(2)	-0.1195(2)	0.6195(2)	1	1.10(5)
S3	4*a*	0	0	1	0.063(9)	2.95(5)

Table S 17: Values obtained from fitting of impedance spectra. Temperaturedependant resistances R aswell as quasi capacitances Q. All capacitances are in the pF range indicating bulk processes. For higher x the bulk process could not be resolved well, to the extend of not being fitted at all (corresponding to empty cells in the table).

$Li_{6+x}P_{1-x}Ge_xS_5I$	0.10	0.15	0.20	0.25	0.30	0.40	0.50	0.60	0.70	0.80
thickness *d* /cm	0.140	0.144	0.250	0.235	0.130	0.220	0.200	0.215	0.130	0.230
Fitting results										
Temperature / K	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω	R_{bulk} / Ω
253	358145	71700	150060	20354	1672	1272	905	363	227	897
263	190745	40300	82916	12811	1166	878	608	242	141	601
268	140430	30100	62440	10020	961	716	505	200	121	483
273	104520	23000	47780	7974	805	593	424	166	100	398
283	60403	14000	28486	5279	588	423	311	120	70	270
293	36013	8630	17580	3543	433	314	232	89	51	196
298	29665	6930	14726	2964	377	275	206	79	45	169
303	23670	5580	11984	2483	329	241	185	70	40	146
313	15142	3700	7929	1770	255	188	147	55	31	113
323	9884	2500	5324	1275	200	149	119	44	24	89
333	6626	1730	3667	938	159	119	97	35	19	71
298	27517	6590	13336	2827	364	265	198	76	44	166
Quasi-Capacitances										
***Q*(253 K) / pF·cm^{-2}**	29	30	29	28	39	41	46	36	36	35
***Q*(298 K) / pF·cm^{-2}**	28	29	27	26	39	47				
***Q*(333 K) / pF·cm^{-2}**	28	28	26	28						

Nuclear magnetic resonance.

The relaxation rate $R_1=1/T_1$ in the simplest case depends on temperature in the following way: if the motional frequency τ_c^{-1} differs a lot from the Larmor frequency ω_L of the nucleus at a given magnetic field, the relaxation rate is small and upon approaching the match condition ($\tau_c^{-1} \approx \omega_L$) the R_1 value increases reaching its maximum. The dependence in the first approximation can be described by the following equation:

$$R_1 = \frac{1}{T_1} \sim \frac{\tau_C}{1 + (\omega_L \tau_C)^2} \qquad \text{Eq. (3)}$$

where τ_C is a correlation time of motion which changes with temperature (T) according to the Arrhenius law:

$$\tau_C = \tau_0 \cdot exp\left(-\frac{E_a}{k_B T}\right) \qquad \text{Eq. (4)}$$

Here k_B is the Boltzmann constant. Figure 6d shows the result of the relaxation time experiments. The sample with $x = 0.25$ reveals different slopes for both flanks and this phenomenon might be attributed to the co-existence of two types of motion. In this case, two overlapping contributions have to be considered:

$$R_1 \sim p_1 \cdot \frac{\tau_1}{1 + (\omega_L \cdot \tau_1)^2} + (1 - p_1) \cdot \frac{\tau_2}{1 + (\omega_L \cdot \tau_2)^2} \qquad \text{Eq. (5)}$$

Thus, by analysis of the relaxation behaviour it is possible to distinguish between two different dynamical processes occurring on different time scales (τ_1 and τ_2). All T_1-defined dynamical parameters are listed in the Supporting Information (Table S18).

Table S 18:Dynamical parameters as defined from T1 relaxation analysis obtained by nuclear magnetic resonance experiments.

Sample	T_{max}	E_a^{LT}	E_a^{HT}	$K_{exchange}$
$x = 0$	315 K	0.19±0.005 eV		$3.3 \cdot 10^8$ s^{-1}
$x = 0.25$	348 K	0.11±0.005 eV	0.21±0.007 eV	$1.6 \cdot 10^8$ s^{-1}
$x = 0.6$	328 K	0.16±0.003 eV		$2.8 \cdot 10^8$ s^{-1}

Impedance spectra of sintered $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$.

To corroborate the high ionic conductivity, impedance spectra were also collected on sintered samples. Therefore, the isostatically pressed pellets were rapid annealed in a vacuum sealed quartz ampoule for ten minutes at 550 °C (823 K) and impedance spectra were collected using different measurement setups and cell constants to confirm the obtained values:

(1) Standard Setup as described in the manuscript ($l_{\text{thickness}} = 0.17$ cm, $r_{electrode} = 0.3$ cm). Impedance was measured in the frequency range from 7 MHz to 100 mHz.

(2) reduced cell constant ($l_{\text{thickness}} = 0.17$ cm, $r_{electrode} = 0.125$ cm). Impedance was measured in the frequency range from 7 MHz to 100 mHz.

(3) Novocontrol Setup (impedance analyzer Novocontrol Technologes, Alpha-AN) to increase the frequency range ($l_{\text{thickness}} = 0.21$ cm; $r_{electrode} = 0.3$ cm). Impedance was measured in the frequency range of 20 MHz to 50 mHz.

The observed standard deviation between the different measurement setups and cell constants stems from the uncertainty of the fitting procedure, leading to a reliability of the ionic conductivity to 18.4 ± 2.7 mS cm^{-1}.

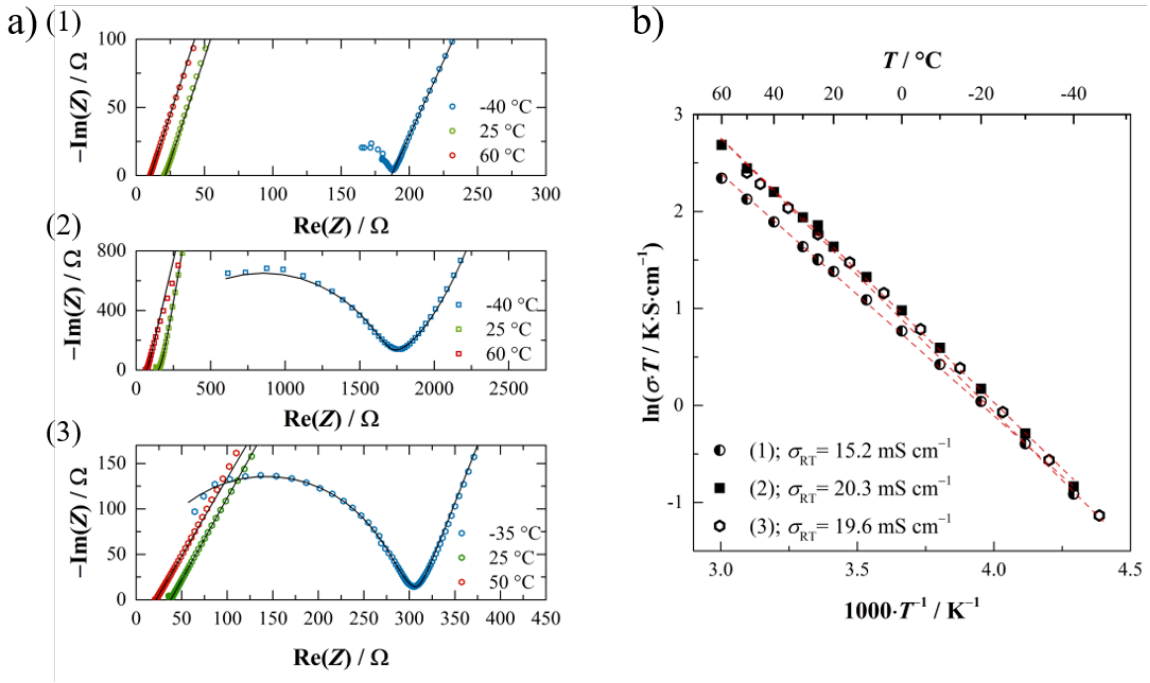

Figure S2: a) Impedance Spectra of the different Setups at different Temperatures. b) Arrhenius Plot of the Impedance results with indicated RT conductivity.

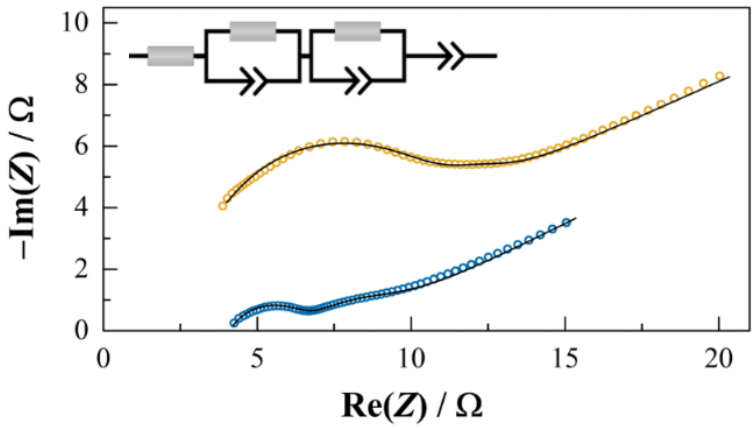

Figure S3: *Nyquist representation of the impedance spectrum of the all-solid-state battery at 60 °C after the initial charge (blue) and after 50 cycles (orange) with offset. The points represent the measured data and the black solid line indicates the fit of the data using the equivalent circuit shown as inlay (top left).*